QUANTUM MONTE CARLO ALGORITHMS FOR DIAGRAMMATIC VIBRATIONAL STRUCTURE CALCULATIONS

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Convergent hierarchies of theories for calculating many-body vibrational ground and excited-state wave functions, such as Møller-Plesset perturbation theory or coupled cluster theory, tend to rely on matrix-algebraic manipulations of large, high-dimensional arrays of anharmonic force constants, tasks which require large amounts of computer storage space and which are very difficult to implement in a parallel-scalable fashion. On the other hand, existing quantum Monte Carlo (QMC) methods for vibrational wave functions tend to lack robust techniques for obtaining excited-state energies, especially for large systems. By exploiting analytical identities for matrix elements of position operators in a harmonic oscillator basis, we have developed stochastic implementations of the size-extensive vibrational self-consistent field (MC-XVSCF) and size-extensive vibrational Møller-Plesset second-order perturbation (MC-XVMP2) theories which do not require storing the potential energy surface (PES). The programmable equations of MC-XVSCF and MC-XVMP2 take the form of a small number of high-dimensional integrals evaluated using Metropolis Monte Carlo techniques. The associated integrands require independent evaluations of only the value, not the derivatives, of the PES at many points, a task which is trivial to parallelize. However, unlike existing vibrational QMC methods, MC-XVSCF and MC-XVMP2 can calculate anharmonic frequencies directly, rather than as a small difference between two noisy total energies, and do not require user-selected coordinates or nodal surfaces. MC-XVSCF and MC-XVMP2 can also directly sample the PES in a given approximation without analytical or grid-based approximations, enabling us to quantify the errors induced by such approximations.